(12) UK Patent Application (19) GB (11) 2 177 711 A

(43) Application published 28 Jan 1987

(21) Application No 8602869

(22) Date of filing 5 Feb 1986

(30) Priority data
(31) 709547 (32) 8 Mar 1985 (33) US

(51) INT CL⁴
C09K 7/06 C08K 5/52 C08L 1/26

(52) Domestic classification (Edition I):
C3V AX BX
C3W 121
E1F GP
U1S 1248 1269 C3V E1F

(56) Documents cited
None

(58) Field of search
C3V

(71) Applicant
NL Industries Inc

(Incorporated in USA–New York)

New York, State of New York, United States of America

(72) Inventors
James A Pelezo
Garry E Corbett Jr
Donald R Siems

(74) Agent and/or Address for Service
Michael Burnside & Partners,
2 Serjeants' Inn, Fleet Street, London EC4Y 1HL

Reprinted front page

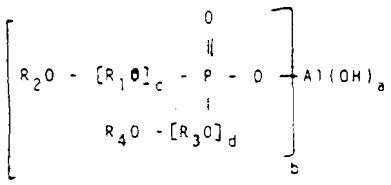
(54) Liquid polymer containing compositions for thickening aqueous mediums

(57) Liquid, water-dispersable, acid-soluble compositions, suitable for thickening aqueous compositions, especially brines used in oilfield operations comprise

(a) hydroxyethyl cellulose (HEC),

(b) an oil base liquid, and

(c) a gelling agent selected from aluminium phosphate compounds of the formula



wherein

a=0 to 2,

b=1 to 3,

the sum of $a+b=3$,

one of c and d is 1 to 5 and the other is 0 to 5,

R_1 and R_3, which may be the same or different, are alkylene, alkenylene or alknylene provided that at least one is $-CH_2CH_2-$ or $-CH_2CH(CH_3)-$, and R_2 and R_4, which may be the same or different, are H, alkyl, alkenyl or alkynyl having 1 to 18 carbon atoms, R_1 and R_2 together contain 1 to 24 carbon atoms, R_3 and R_4 together contain 1 to 20 carbon atoms, and the number of carbon atoms in at least one of the groups R_1, R_2, R_3 and R_4 is at least 6.

Optionally, a surfactant may be included to retard settling and hardpacking of the HEC.

Formulae in the printed specification were reproduced from drawings submitted after the date of filing, in accordance with Rule 20(14) of the Patents Rules 1982

GB 2 177 711 A

SPECIFICATION

Liquid polymer containing compositions for thickening aqueous mediums

The present invention relates to liquid, polymer containing compositions for use as thickening agents for aqueous media and, more particularly, to liquid, polymer containing compositions which can be used to viscosify brines to provide thickened aqueous well drilling and treating fluids.

The use of polymers such as hydroxyethyl cellulose (HEC) in fluids, e.g. brines, used in well drilling and treating fluids to improve viscosity, solids removal and/or filtration control has met with much success in past years. It is known, however, that the direct application of the dry powder form of these powders results in the formation of "fish eyes," i.e. unhydrated lumps of polymer, which can result in operational problems, such as blinding of shaker screens and formation plugging. These problems can be minimized by adding the polymer in the form of a solution, colloid or other uniform suspension dispersed in a non-solvent carrier medium, such as an oil-base liquid, e.g. diesel oil or Kerosene. In Trinidad Patent 3 of 1981 there is disclosed one such HEC formulation which has met with great success. The composition disclosed in the aforementioned co-pending application suffers, however, from the disadvantage that if the formulation is stored under static conditions for an extended period, some undesirable settling and hard packing of the HEC results. Redispersion of the HEC is time-consuming, requires special equipment, and therefore is generally not conductive to on-site drilling, workover or completion operations.

Another disadvantage of the composition disclosed in the aforementioned application is that the composition, because it contains clay, is not completely acid-soluble. As is well known, in the case of fluids used in workover and completion applications, it is desirable, and in some cases essential, that the fluid be acid-soluble, so that it can be displaced from the formation if necessary without damaging the formation.

It is therefore an object of the present invention to produce an improved, liquid polymer containing composition useful in the thickening of aqueous media.

A further object of the present invention is to provide an improved aqueous well treating or drilling fluid.

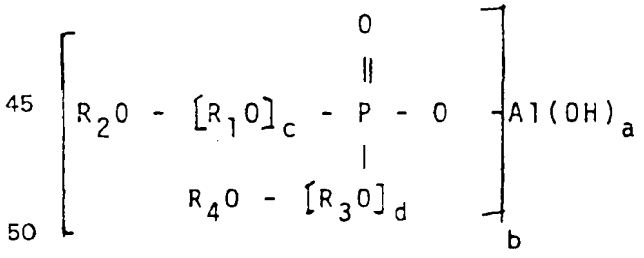
Still another object of the present invention is to provide a liquid, polymer containing composition which can be mixed with oil-filled brines and the like to form thickened aqueous well drilling and treating fluids and which is essentially acid soluble.

The above and other objects of the present invention will become apparent from the description given herein and the appended claims.

In accordance with the present invention, there is provided a liquid water-dispersible thickening composition which comprises:

(a) hydroxyethyl cellulose (HEC),

(b) a gelling agent selected from aluminum phosphate compounds of the formula



wherein

a=0 to 2, and

b=1 to 3,

the sum of $a+b=3$, one of c and d is 1 to 5 and the other is 0 to 5, R_1 and R_3, which may be the same or different, are $-CH_2CH_2O-$ or $-CH_2CH(CH_3)O-$, and R_2 and R_4, which may be the same or different, are hydroxy alkyloxy, alkenyloxy or alkynloxy having 1 to 18 carbon atoms, R_1 and R_2 together contain 1 to 24 carbon atoms, R_3 and R_4 together contain 1 to 20 carbon atoms, and the number of carbon atoms in at least one of the groups R_1, R_2, R_3 and R_4 is at least 6.

The compositions according to the present invention can be used for thickening aqueous liquids such as fresh water, oil–field brines and the like to provide well drilling and treating fluids, e.g. completion and workover fluids. The oil-based liquid is generally speaking a hydrocarbon in which the HEC is substantially non-swellable. In a particularly preferred embodiment of the present invention, there is included a surfactant which aids in preventing settling and hard

packing of the HEC. The liquid, polymer containing compositions, when mixed with aqueous liquids, particularly oil-field brines, provide ideal well drilling or treating fluids.

The novel, liquid polymer containing compositions of the present invention utilize hydroxyethyl cellulose (HEC) as the primary component to effect thickening of the aqueous medium. Hydroxyethyl cellulose is a high yield, water-soluble nonionic polymer produced by treating cellulose with sodium hydroxide followed by reaction with ethylene oxide. Each anhydroglucose unit in the cellulose molecule has three reactive hydroxy groups. The average number of moles of ethylene oxide that become attached to each anhydroglucose unit in cellulose is called "moles of substituent combined". In general, the greater the degree of substitution, the greater the water solubility. While HEC having a mole substitution level as low as 1.5 can be used, it is preferable to use HEC having mole substitution level of 1.8 or greater, especially 2.5 and greater. It will be understood that the particular HEC chosen will depend upon the type of liquid polymer composition, and ultimately the type of well drilling or treating fluid, desired. For example, so called surface treated HEC such as described in U.S. Patents 3,455,714; 2,879,268 and 3,072,035 can be used with advantage. Such surface teated HEC exhibits greater dispersability in the composition. The HEC will be present in the liquid polymer-containing composition in amounts from 25 to 55% by weight, based on the total weight of the liquid, polymer-containing composition.

The oil base liquid used in preparing the composition of the present invention, in general, is any hydrocarbon which does not cause significant swelling or thickening of the HEC. Exemplary oil base liquids include liquid aliphatic and aromatic hydrocarbons, particularly those containing five to ten carbon atoms, diesel oil, kerosene, petroleum distillates, petroleum oils, mineral oil, and the mixtures thereof. Generally speaking, the oil base liquid will be non-polar and will have a low pour point. A particularly preferred oil base liquid is a paraffin base oil of the mineral seal or white mineral oil type, which is substantially free of aromatic compounds. Such oils, since they are biodegradable, are environmentally safe and find particular utility in offshore operations. The oil base liquid will be present in the composition of the present invention in amounts of from 35 to 75 percent by weight, based on the total weight of the composition, and preferably from 40 to 60 percent by weight, based on the total weight of the composition.

The gelling agent used in the compositions of the present invention is the gelling agent disclosed in U.S. Patent 4,316,810, in which the gelling compounds are generically represented by the structural formula set out above, the various symbols being identified as follows:

where

a=0 to 2

b=1 to 3

c=1 to 5

d=1 to 5

and the sum of a+b=3

R_1O and R_3O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms, or $CH_2CH(CH_3)O$, or CH_2CH_2O or OH, and

R_1O and R_4O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms, and

R_1O and R_2O may differ from each other but shall together contain from 1 to 24 carbon atoms, and R_3O and R_4O may differ from each other but shall together contain from 1 to 20 carbon atoms, provided that at least one of R_1O and R_3O shall be either $CH_2CH(CH_3)O$ or CH_2CH_2O, and provided further that where either R_1O or R_3O is neither $CH_2CH(CH_3)O$ nor CH_2CH_2O, then the respective R_2O or R_4O group otherwise bonded thereto shall be deleted. It will be noted that these definitions vary in some respects from those used in the claims of this Application, but are believed to be equivalent in effect. These gelling agents may sometimes be referred to as aluminium oxaalkyl (or oxaalkyl alkyl) phosphate salts, in which the term "alkyl" is being used in the generic sense to include straight and branched chain, saturated and unsaturated aliphatic hydrocarbon groups.

The amount of the aluminum oxaalkyl phosphate salt, i.e. the gelling agent, utilized in the composition of the present invention will be from 0.15 to 6 weight percent, based on the total weight of the composition. Preferably, at least 0.25 weight percent of the gelling agent is added to the oil base liquid, with the most preferred compositions containing from 0.3 to 2 percent by weight. The gelling agent can be added either as a pre-prepared salt or can be formed in situ. The latter procedure constitutes the preferred method of incorporation of the gelling agent into the thickening composition of the present invention, since better control of the properties of the composition is achieved.

Where in situ formation of the gelling agent is the procedure followed, the phosphoric acid ester precursor is initially added to the oil base fluid in an amount such as to provide the desired amount of gelling agent specified above. An appropriate amount of the sodium aluminate, preferably mixed with sodium hydroxide and water, is then added to the oil base liquid.

Although the compositions of the present invention provide clay free, polymer-containing

compositions which minimize settling and hard packing of the HEC, it is desirable to retard further such settling and hard packing by incorporating a surfactant into the compositions. Non-limiting examples of suitable surfactants include sorbitan, fatty acid esters such as sorbitan monoleate, sorbitan monostearate, sorbitan monopalmitate or sorbitan triestearate; polyoxyethelene sorbitan fatty acid esters such as polyoxyethylene sorbitan monolaurate or polyoxyethylene sorbitan monopalmitate; alkyl aryl sulfanates; and polymeric fatty esters. It will be appreciated that the type and amount of surfactant employed will depend upon the concentration of the HEC, storage time of the polymer composition and other such variables. Generally speaking however, the surfactant will be employed in an amount of from 0.25 to 4% by weight, based on the total weight of the polymer composition.

In preparing the liquid, polymer-containing compositions, and when in situ formation of the gelling agent is employed, the phosphoric acid ester is added to the oil base liquid and stirred followed by addition of the sodium aluminate solution, stirring being continued for a suitable period of time until the reaction between the sodium aluminate and the phosphoric acid ester is complete. Following this, the optional surfactant is added and the mixture is stirred. The HEC is then added and the composition then is thoroughly mixed, with shearing, until the desired viscosity is achieved.

The compositions of the present invention find particular use in the preparation of fluids such as completion fluids and workover fluids. In the preparation of such fluids, the liquid, polymer compositions are mixed with a suitable aqueous medium. While the aqueous medium can comprise fresh water or tap water, the aqueous medium will preferably be one which contains a soluble salt for example, a soluble salt of an alkali metal, and alkaline earth metal, a Group IB metal, a Group IIB metal, or water-soluble salts of ammonia and other anions. In particular, brines containing sodium chloride and/or calcium chloride, when mixed with the liquid polymer compositions herein, make excellent workover fluids. The amount of the water-soluble salt dissolved in the aqueous medium will vary depending upon the desired density of the well drilling or treating fluid. For example, it is common to employ saturated solutions of sodium chloride and/or calcium chloride in preparing such fluids. In preparing aqueous well drilling and treating fluids using the liquid, polymer containing compositions, the amount of the liquid polymer composition added will vary depending upon the viscosity desired. Desirable well drilling and treating fluids can be made by combining an aqueous medium with sufficient liquid, polymer containing compositions such that the final mixture contains from 0.25 to 6 g/litre of HEC.

To illustrate further the invention, the following non-limiting examples are presented. In all cases, the HEC used was Natrasol 250 HHR marketed by Hercules Incorporated.

Example 1

Acid soluble (15 percent aqueous HCl) liquid, polymer compositions of HEC were prepared using No. 2 diesel oil as the oil base liquid. The aluminum oxaalkyl phosphate salt was obtained, in situ, by combining a phosphoric acid ester, as described above, and sold under the trade name ASP-162 by Nalco Chemical Company with an aqueous sodium hydroxide solution of sodium aluminate sold under the trade name ASP-200 by Nalco Chemical Co. Tables I and II below show various formulation (Table I) and rheological properties thereof (Table II).

TABLE I

Weight Percentage of Components

Sample No.	Diesel	HEC	Phosphoric Acid Ester	Sodium Aluminate	Comment
1	52.0	45	4.6	0.40	Good suspension Poor pourability
2	51.0	45	3.7	0.30	Good suspension Fair pourability
3	53.1	45	1.5	0.15	Fair suspension Good pourability
4	53.6	45	1.0	0.50	Poor suspension
5	54.1	45	0.1	0.05	Hard packing

TABLE II

Sample No.	θ 600	θ 300	PV	AV	YP	Comment
1	300	275	-	-	-	Good suspension Poor Pourability
2	290	185	105	145	80	Good suspension Fair pourability
3	197	150	47	98	103	Fair suspension Good pourability
4	163	99	64	81	35	Poor suspension
5	140	87	53	70	34	Poor suspension

Example 2

A series of brines, viscosified with a liquid polymer composition designated as Sample No. 2 in Example 1 was compared with a like series of brines viscosified with the liquid polymer composition disclosed in Trinidad Patent 3 of 1981 (Prior Liquid Polymer). The rheology of the samples was evaluated using a FANN model 35A viscometer. The results are shown in Tables II–VI below.

TABLE III

Plastic Viscosity Produced by Sample 2 of Example 1

	Amount in gram/litre					
Medium	*Blank*	*2.86*	*5.72*	*8.58*	*11.44*	*14.3*
Water	1.0	12.0	15.0	27.0	36.0	—
NaCl (31.46 g/l)	2.0	8.0	9.0	13.0	18.0	41.0
NaBr (31.46 g/l)	1.5	4.0	12.0	20.0	49.0	64.0
$CaCl_2$ (33.18 g/l)	8.0	8.5	11.0	14.5	27.5	52.5
$CaBr_2$ (40.61 g/l)	7.0	10.0	10.0	10.0	12.0	15.0
KCl (27.74 g/l)	3.5	4.0	8.0	14.0	18.0	20.0
$CaCl_2/CaBr_2$ (35.75 g/l)	9.0	14.0	11.5	14.0	14.5	16.0
$CaCl_2/CaBr_2/ZnBr_2$ (51.48 g/l)	23.0	21.0	19.5	20.0	24.0	20.0
$ZnBr_2$(54.91 g/l)	30.0	23.0	23.0	23.0	23.0	23.0

TABLE IV

Plastic Viscosity Produced by Prior Liquid Polymer

	Amount in gram/litre					
Medium	*Blank*	*2.86*	*5.72*	*8.58*	*11.44*	*14.3*
Water	1.0	7.0	10.0	13.0	19.0	25.0
NaCl	2.0	9.0	13.0	17.0	20.0	25.0
NaBr	1.5	8.0	11.0	18.0	17.0	28.0
$CaCl_2$	8.0	13.5	22.0	26.0	32.0	35.0
$CaBr_2$	7.0	10.0	9.5	13.0	12.5	14.0
KCl	3.5	6.5	8.5	12.5	15.0	20.0
$CaCl_2/CaBr_2$	9.0	12.0	14.0	17.5	20.5	24.0
$CaCl_2/CaBr_2/ZnBr_2$	23.0	20.0	20.5	22.0	21.5	24.0

TABLE V

Yield Point Produced by Sample 2 of Example 1

	Amount in gram/litre					
Medium	*Blank*	*2.86*	*5.72*	*8.58*	*11.44*	*14.3*
Water	1.0	10.0	42.0	83.0	154.0	—
NaCl	2.0	3.0	9.0	18.0	41.0	—
NaBr	1.0	4.0	12.0	20.0	49.0	64.0
$CaCl_2$	1.0	3.5	11.0	14.5	27.5	52.5
$CaBr_2$	3.0	3.0	2.0	2.0	3.0	5.0
KCl	1.5	2.0	4.0	13.0	26.0	46.0
$CaCl_2/CaBr_2$	0.0	1.0	3.5	2.5	2.0	2.0
$CaCl_2/CaBr_2/ZnBr_2$	3.0	0.0	0.0	0.0	0.0	3.0
$ZnBr_2$	0.0	2.0	3.0	4.0	5.0	6.0

TABLE VI
Yield Point Produced by Prior Liquid Polymer

	Amount in gram/litre					
Medium	*Blank*	*2.86*	*5.72*	*8.58*	*11.44*	*14.3*
Water	1.0	3.0	9.0	12.0	55.0	61.0
NaCl	2.0	1.0	7.0	19.0	29.0	44.0
NaBr	1.0	5.0	8.0	28.0	48.0	64.0
$CaCl_2$	1.0	1.5	7.0	19.0	40.0	75.0
$CaBr_2$	3.0	1.0	2.0	2.0	4.5	5.5
KCl	1.5	2.0	6.5	13.0	26.0	41.0
$CaCl_2/CaBr_2$	0.0	0.0	3.5	4.5	6.0	10.0
$CaCl_2/CaBr_2/ZnBr_2$	3.0	0.0	1.0	1.5	3.0	1.0

A comparison of the apparent viscosity of Sample No. 2 with the Prior Liquid Polymer composition showed that both were equally effective in viscosification of the brines listed in Tables III–VI above.

To determine the acid solubility of the polymer-containing compositions, samples of 2ml each of Sample No. 2 were placed into each of three, 100ml aqueous solutions of 15% HCl and stirred with heating. In all cases, the solute dispersed and solution occurred, leaving a non-viscous clear solution. It can thus be seen from Tables III-VI that the liquid, polymer compositions of the present invention, which are free of clay and therefore completely acid soluble, are as effective in viscosifying typical oil field brines as the Prior Liquid Polymer composition, which contains a clay-based gelling agent and which has been successfully used commercially in typical oil field operations such as workovers and completions. As noted above, solution in acid is an important feature, particularly in completion operations, since residual, non-dissolved solids in the fluids can damage the producing formation.

Example 3

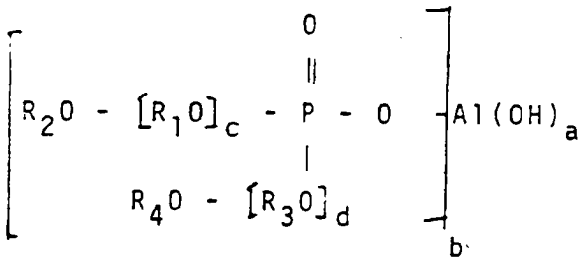
The addition of a surfactant in retarding settling and hard packing of HEC in a liquid, polymer composition (Sample A) containing no surfactant is compared with a liquid, polymer-containing composition (sample B) having substantially the same composition as Sample A, but containing, in addition, a polymeric fatty ester surfactant marketed as Solsperse 6000 by ICI. Both samples are static aged at 49°C for 20 days. It is observed that whereas significant settling and hard packing of HEC occurs in Sample A, there is little or no settling or hard packing of HEC in Sample B.

Example 4

A liquid, polymer-containing composition was formulated by mixing together 53.44% by weight of a substantially aromatic-free mineral oil, sold under the trade name Mentor 28 by Exxon, 0.48% by weight of a phosphoric acid ester sold as ASP-166, 0.08% by weight of a sodium aluminate/sodium hydroxide solution sold as ASP-200, 1.00% by weight of a polymeric fatty ester surfactant sold as Solsperse 6000 and 45.00% by weight of HEC. The formulation thus produced flowed freely and exhibited no settling or hard packing after static aging at 49°C for one week, the composition also remaining pourable after one week. The composition effectively viscosified 28.6 g/l NaCl brine and 33.18 g/l $CaCl_2$ brine. This example shows that the present invention permits the preparation of environmentally-safe, clay-free, acid-dispersible viscosifying compositions for brines. The liquid, polymer-containing composition, since they are stable, i.e. minimal settling or hard packing, can be stored and used more easily than formulations in which the HEC settles and hard packs requirinf cumbersome and generally unavailable mixing equipment.

CLAIMS

1. A liquid water-dispersible thickening composition which comprises:
(a) hydroxyethyl cellulose (HEC),
(b) an oil base liquid, and
(c) a gelling agent selected from aluminum phosphate compounds of the formula



wherein

a=0 to 2, and

b=1 to 3,

the sum of $a+b=3$, one of c and d is 1 to 5 and the other is 0 to 5, R_1 and R_3, which may be the same of different, are $-CH_2CH_2O-$ or $-CH_2CH(CH_3)O-$, and R_2 and R_4, which may be the same or different, are hydroxy alkyloxy, alkenyloxy or alkynyloxy having 1 to 18 carbon atoms, R_1 and R_2 together contain 1 to 24 carbon atoms, R_3 and R_4 together contain 1 to 20 carbon atoms, and the number of carbon atoms in at least one of the groups R_1, R_2, R_3 and R_4 is at least 6.

2. A composition as claimed in Claim 1 which further comprises a surfactant.

3. A composition as claimed in Claim 2 which comprises from 0.25 to 4% by weight, based on the total weight of said composition of said surfactant.

4. A composition as claimed in any preceding claim which comprises from 25 to 55% by weight, based on the weight of said composition of HEC.

5. A composition as claimed in any preceding claim which comprises from 15 to 6.0% by weight, based on the total weight of said composition of said gelling agent.

6. A composition as claimed in any preceding claim which comprises from 35 to 75% by weight, based on the total weight of said composion of said oil base liquid.

7. A composition as claimed in any preceding claim wherein said oil base liquid is a liquid aliphatic or aromatic hydrocarbon, petroleum distillate, petroleum oil, diesel oil, kerosene, substantially aromatic-free mineral oil, or a mixture thereof.

8. A composition as claimed in Claim 1 and substantially as hereinbefore described with reference to any of the Examples.

9. A thickened aqueous fluid which comprises water and a composition as claimed in any of the preceding claims.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1987, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.